

Audit of Data Quality Report

Data Associated with Pavillion Ground Water Investigation Phase V April 2012 Sampling Event

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July 12, 2012
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Phase V April 2012 Sampling Event

ADQ performed by Neptune and Company, Inc.

1. INTRODUCTION:

This Audit of Data Quality (ADQ) was performed per the NRMRL SOP, *Performing Audits of Data Quality (ADQs)*, to verify that requirements of the Quality Assurance Project Plan (QAPP) were properly implemented for the analysis of samples submitted to laboratories identified in the QAPP associated with this project. The associated QAPP for this case study was entitled *Ground-Water Investigation in Pavillion, Wyoming (QA ID G-14478, Revision 6, February 17, 2012)*.

2. ADQ APPROACH:

Complete data packages were provided to the auditors for the Pavillion Wyoming April 2012 sampling event. A complete data package consists of the following: sample information, method information, data summary, laboratory reports, raw data including QC results, and data qualifiers. The QAPP was used to identify data quality indicator requirements and goals, and a checklist was prepared based on the types of data collected. Metals data were reviewed using revised acceptance criteria dated May 22, 2012.

The data packages were reviewed against the checklist by tracing a representative set of the data in detail from raw data and instrument readouts through data transcription or transference through data manipulation (either manually or electronically by commercial or customized software) through data reduction to summary data, data calculations, and final reported data. All calibration and QA/QC data were reviewed for all data packages identified in Table 1. Auditors also reviewed the final data summary (Excel Spreadsheet, "*Pavillion Apr2012 QA Summary v0.xlsx*") to determine if data had been accurately transcribed from lab summary reports and appropriately qualified based on lab and field QC results.

The critical analytes, as identified in the QAPP (Table 9), are Gasoline Range Organics (GRO); Diesel Range Organics (DRO); Semivolatile Organic Compounds (SVOCs); Volatile Organic Compounds (VOCs) of ethanol, isopropyl alcohol, tert-butyl alcohol, naphthalene, benzene, toluene, ethylbenzene, and xylene; major cation potassium, major anion chloride. Note, the VOC analysis performed by Region 8 does not include ethanol, isopropyl alcohol, or tert-butyl alcohol.

Also included in this ADQ are the following analytes: dissolved inorganic and organic carbon; dissolved gases by GC; stable oxygen and hydrogen isotopes of water; low molecular weight

acids by HPLC; stable carbon isotope ratio of dissolved inorganic carbon, stable carbon and hydrogen isotope ratios of dissolved methane; tritium; MBAS (methylene blue active substance), glycols; ethoxylated alcohols and alkylphenols; acrylamide; methanol, ethylene glycol, and propylene glycol.

Table 1 below summarizes the samples and laboratory analyses reviewed as part of this Version 1 ADQ Report. Future reports will incorporate the remaining analytical suites discussed above that are not included in Table 1 below.

Sample Identification	Laboratory	Analyses (all samples)
PGDW05-0412	EPA, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center Shaw Lab at Ada, OK	Metals and major cations (calcium, magnesium, potassium, sodium, arsenic, selenium, uranium), headspace analysis of VOC (critical), stable oxygen and hydrogen isotopes of water, low molecular weight acids by HPLC, dissolved gases of methane, ethane, propane and n-butane.
PGDW20-0412		
PGDW20d-0412		
PGDW23-0412		
PGDW30-0412		
PGDW50-0412		
PGPW02-0412		
EPAMW02-0412-1	TestAmerica Inc, Savannah Georgia	Methylene Blue Active Substances (MBAS)
EPAMW02-0412-2		
EPAMW01-0412		
EPAMW01d-0412	Isotech Laboratories, Champaign Illinois	Stable carbon isotope ratio of DIC, stable carbon and hydrogen isotope ratios of dissolved methane, tritium
EPAMW01-0412-2		
EPAMW01-0412-3		
EPAMW01-0412-4		
EPAMW01-0412-5	EPA, Region VIII Golden Colorado	Purge and trap VOCs (those critical analytes that were reported), SVOCs (still be audited), GRO (still be
EPAMW01-0412-6		
EPAMW01-0412-7		
EPAMW01-0412-8		

EPAMW01-0412-9		audited), DRO (still be audited)
EPAMW01-0412-10		
Associated Field Blanks, Equipment Blanks, and Trip Blanks	EPA, Region III, Environmental Science Center at Ft. Meade, MD	Glycols
	RSKERC General Parameters Lab, Ada, OK	DOC, DIC, anions of chloride and sulfate
	ALS Laboratories	methanol, ethylene glycol, propylene glycol

Table 1. Samples and associated laboratories under this ADQ Version 1 Report.

3. ADQ REPORT CONTENT:

This ADQ report includes the audit approach, the audit results, and the completed ADQ checklist.

4. ADQ RESULTS:

ADQ Definitions

To assist in the interpretation of this ADQ report, the following definitions are provided:

Deficiency – an identified deviation from project QA/QC requirements.

Finding – a deficiency that has or may have a significant effect on the quality of the reported results. A corrective action response is required.

Observation – a deficiency that does not have a significant effect on the quality of the reported results. A corrective action response is required.

Additional Comment – an issue that is not a deficiency but may need to be considered to improve or clarify current processes. A corrective action response is not required.

ADQ Summary

The QA/QC requirements specified in the associated QAPP have been met or the data appropriately qualified, with the following exceptions. The completion of appropriate corrective actions will minimize any significant impact to the data summarized for reporting.

Observations

1. **Field and Equipment Blanks.** Section 4.1.d of the QAPP indicates that a Field Blank and Equipment blank will be collected on every day of sampling. For all of the analyses reviewed in this ADQ, this requirement was not met. In most cases samples were collected on seven different days, but only 3-4 Field and Equipment (where applicable) Blanks were collected.
 - a. The DOC result for sample PGDW05-0412 should be flagged FB due to the associated Field Blank that is not less than ten times the concentration of this sample. It is noted that the associated Equipment Blank was a non-detect.
 - b. The total selenium values for several samples (PGDW05-0412, PGDW20-0412, PGDW20d-0412, EPAMW01-0412-10, and EPAMW01d-0412-10) are less than ten times the associated Field Blanks. These samples should be flagged FB.
 - c. The Field Blank and Trip Blank collected on 4/18/2012 had low levels of methane, ethane, and propane. Sample PGDW05-0412 also collected on this same date had detectable levels of methane that are not greater than ten times the concentration in these blanks. The methane value for this sample should be qualified EB and FB. However, the final summary spreadsheet does include the FB and EB flags for two samples collected on 4/19 and 4/20. It is unclear why these flags have been added since there are no Field or Equipment Blanks for these days.

Recommended Correction Action. (a) In the summary spreadsheet, qualify all results above MDL for which there is not a corresponding FB and or/ EB. Existing qualifiers do not cover this issue, so a new one may be created. The field crews need to be sure that all field

QC samples are collected. Each day of sampling a Field Blank and Equipment Blank are to be collected. How this impacts sample data interpretation needs to be addressed in the QAQC writeup. (b) Flag the samples identified above (for DOC and total Se) with “FB” to indicate their values are less than ten times the associated Field Blank value. (c) Removed the FB and EB flags for samples PGDW50-0412 and PGPW02-0412 unless these samples are associated with Field Blank and Equipment Blank collected on 4/18/2012 based upon field notes. Add these same flags to sample PGDW05-0412 for methane.

Corrective Action Performed.

2. **Metals/major cations via ICP-OES:** As outlined in the table below (checklist item 10), not every element that is reported was included in a continuing calibration check standard to bracket all samples. It is noted that the second source standard analyzed prior to the samples did contain all reported elements and was within the acceptance criteria, and when the CC was analyzed it did meet the acceptance criteria. Therefore there are calibration checks that bracket the samples, but in several instances the beginning check is from the second source, not the CC check standards. These checks indicate the instrument was under control, but that the exact SOP requirements were not met with respect to continuing calibration checks.

The matrix spike samples analyzed by ICP-OES for both the total and the filtered samples did not include the element sodium. In addition, only one of two MS samples for total metals/cations included the element sulfur. The post-digestion spike of sample PGDW30-0412 did not include sulfur. For the filtered MS samples, only one of two samples included silicon and sulfur. The MS of sample EPAMW01-0412-10 did not include these elements.

Recommended Correction Action. (a) The laboratory needs to be instructed to ensure that the analytical runs include a CC that brackets all samples with all elements that are reported and the matrix spike combinations needs to include all elements. (b) The following samples need to be flagged J2 due to incomplete CCC frequency. For Technical Directive 8ME801SF, the nineteen total samples that need to be flagged for silicon, sulfur, phosphorous are:

FieldBlk 1	PGDW05-0412
EquipBlk 1	FieldBlk 3
PGDW20-0412	PGDW50-0412
	PGPW02-0412
PGDW20d-0412	

	EPAMW02-0412-2
EPAMW02-0412-1	
	FieldBlk 4
PGDW23-0412	EquipBlk 4
PGDW30-0412	EPAMW01-0412
FieldBlk 2	EPAMW01d-0412
EquipBlk 2	EPAMW01-0412-10

For this same TD, the dissolved samples (analyzed on 4/30/2012) that need to be flagged J2 due to incomplete CCC frequency for sodium are:

EquipBlk 2	FieldBlk 1
PGDW05-0412	EquipBlk 1
FieldBlk 3	PGDW20-0412
PGDW50-0412	PGDW20d-0412
PGPW02-0412	EPAMW02-0412-1

EPAMW02-0412-2	PGDW23-0412
FieldBlk 4	PGDW30-0412
EquipBlk 4	FieldBlk 2
EPAMW01-0412	
EPAMW01d-0412	

For this same TD, the dissolved samples (analyzed on 5/1/2012) that need to be flagged J2 due to incomplete CCC frequency for potassium are:

EPAMW01-0412-2	EPAMW01-0412-7
EPAMW01-0412-3	EPAMW01-0412-8
EPAMW01-0412-4	EPAMW01-0412-9
EPAMW01-0412-5	EPAMW01-0412-10
EPAMW01-0412-6	

Corrective Action Performed.

3. **Region 3 Glycols Quality Controls.** Analyte recoveries for continuing calibration verification (CCV) / blank spikes (BS) fell below the percent recovery limits for low BS 5 ppb analyzed on 4-20-21/2012, low BS 5 ppb analyzed on 5/1-2/2012, low BS 10 ppb analyzed on 5/2-3/2012 and low BS 5 ppb analyzed on 5/2-3/2012. For details about the percent recoveries for the affected analytes, please see #11 below in the ADQ checklist table. Note the quantification limit was raised from 5 to 10 ppb for tetraethylene glycol and triethylene glycol based on the low blank spike recoveries at the 5 ppb level.

Matrix Spike 1 and its duplicate (MS1/MSD1) were below the 70-130% limits for all 4 analytes and the RPD was above 25% for 2-butoxy ethanol and triethylene glycol. The laboratory noted these issues and flagged sample results with an "A" in the final report.

Recommended Correction Action. With respect to the CCV/BS issues, non-detect results for all 4 analytes in samples analyzed on 5/2/2012 and 5/3/12 should be qualified as K2 because of the low recoveries in the BSs (10 and 5 ppb), which are equal to the quantification limit. Therefore, all analytes in the following samples should be qualified as K2 in the final summary spreadsheet: EPAMW01-0412-7 (excluding diethylene glycol due to high detect), EPAMW01-0412-10 (excluding diethylene glycol due to high detect), EPAMW01-0412-4 (excluding diethylene glycol due to high detect), EPAMW01d-0412 (excluding diethylene glycol due to high detect). The Case Narrative of the lab report recognizes these QC issues and in some cases analytes are J flagged.

MS1/MSD1 were made from source sample PGDW30-0412. All samples analyzed on the same dates as this MS1/MSD1 (4/20-20/2012) should be qualified as K2 (this includes all 4 analytes) due to the low MS recoveries. Affected samples are: Field Blank 1, Equipment Blank 2, PGDW20-0412, PGDW20d-0412, EPAMW02-0412-1, PGDW23-0412, PGDW30-0412, Field Blank 2, Equipment Blank 2, and PGDW05-0412.

Corrective Action Performed.

4. **DOC MDL Value in the Final Summary Spreadsheet.** The Field Blanks and Equipment blanks in the final summary spreadsheet for DOC use a <0.044 value when the analyte was not detected, this is the MDL for DIC not DOC.

Recommended Correction Action. Confirm the correct MDL for DOC and incorporate this in the final data as a <value.

Corrective Action Performed.

5. **Stable oxygen and hydrogen isotope ratios of water.** For the stable hydrogen and oxygen isotopes of water: The replicate injections of the oxygen isotopes for sample PGDW20d-0412 just exceeded the limits. The difference was 0.11 ‰ for $\delta^{18}\text{O}$, above the criteria of $\leq 0.1\text{‰}$. This sample should be qualified in the final summary spreadsheet with a J6.
- 6.

7. **Stable carbon and hydrogen isotope ratios of dissolved methane:** One laboratory duplicate analysis in Job 17997 of sample EPAMW02-0412-1 exceeded the QAPP Table 10 precision limits of $< 3\text{‰}$ for δDC1 (hydrogen isotopes of methane). The original and duplicate results were -204.6‰ and -208.3‰ respectively with a difference of 3.7‰.

Recommended Correction Action. Sample EPAMW02-0412-1 for stable carbon and hydrogen isotope ratios of dissolved methane should be qualified J6. The laboratory should also re-analyze samples when the precision limits for duplicates exceed 3‰ for δD .

Corrective Action Performed.

8. MBAS Chain-of-Custody, Second Source Standard.
- For Job Number 680-78755-1, that included only sample PGDW50-0412, the chain of custody date and time was not completed. There is a name of receiver, their signature, and affiliation as TestAmerica. The case narrative in the report indicates the sample was received on 4/20/2012.
 - The QAPP indicates that a second source standard is to be included with the MBAS analysis and have recovery of 90-110%. No information on a second source standard was provided by the laboratory. In each set of samples a laboratory control sample (LCS) was analyzed and the recovery of that sample was within these limits with one exception (Job Number 680-79065-1) where the recovery was 89%. However, this job number is associated with a sample that was not reported for this Phase V sampling event (Riverton WY Truck Water).

Recommended Correction Action. (a) The laboratory should be reminded that the chain-of-custody needs to be completed with all information. (b) Because no second source standard was analyzed, all results should be qualified J2. The laboratory needs to be contacted to set up a second source standard check, and the calibration results and second source standard results need to be reported.

Corrective Action Performed.

9. **Reg 8 VOCs, Second Source Standard Checks.** The initial calibrations were not immediately verified by a second source calibration verification (ICV) standard containing all analytes. Instead, a mixture of SRMs was analyzed after the initial calibrations. Because of the lack of complete ICVs, all sample results are qualified as estimated and are suitable for screening

purposes only.

Recommended Correction Action.

Corrective Action Performed.

ADQ CHECKLIST

Number	ADQ Issue	Yes	No	NA	Comments
Sample Information					
1	Are samples uniquely identified and their identification correctly transcribed throughout the data package to the summary of results?	Yes			For Version 2: yes for headspace (RSK) and P&T (Region 8) VOCs, water isotopes, dissolved gases, anions, MBAS,
2	Does sample collection documentation indicate that samples were collected as described in the QAPP, and the schedule and volumes in the planning documentation?	Yes, this also includes the samples sent to EPA, Ada Oklahoma but associated with analyses not yet fully audited.			For Version 2: yes for headspace (RSK) and P&T (Region 8) VOCs, water isotopes, dissolved gases, anions, MBAS,
3	Does sample collection documentation indicate appropriate preservation?	Yes 13			For Version 2: yes for headspace (RSK) and P&T (Region 8) VOCs, water isotopes, dissolved gases, anions, MBAS
4	If applicable, is chain-of-custody	Yes, this also			For Version 2: yes for headspace (RSK) and

